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A STUDY OF NOVEL ION EXCHANGE RESINS AND ELECTRODIALYSIS IN THE REMOVAL OF CONTAMINANTS FROM WASTE WATERS

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Cincinnati, Ohio

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U. S. Department of Health, Education, and Welfare
Public Health Service
Division of Water Supply and Pollution Control
Advanced Waste Treatment Research Program
Robert A. Taft Sanitary Engineering Center
Cincinnati 26, Ohio

by

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Cambridge, Massachusetts

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1.0 FOREWORD

It was the purpose of this contract to develop novel ion exchange resins and to conduct a study of the use of ion exchange membranes in electrodialysis cells as an advanced waste treatment.

The scope of the contract included two phases, which are described below.

Phase I

(1) Attempt to synthesize ion exchange resins of high porosity and large pore size, to achieve high exchange capacity, eliminate surface fouling and allow comparatively easy regeneration. Achievement of these goals was sought by:

a) The addition of non-reactive materials during polymerization, with subsequent extraction of the non-reactive materials from the ion-exchange polymer matrix.

b) Decreasing the degree of cross-linking of the ion exchange resin.

(2) Determine the removal efficiencies (for organic and inorganic refractory materials found in secondary sewage effluent, including COD, ABS, and salts) obtainable with the various newly developed resins.

(3) Study the techniques necessary for the repeated regeneration of the various resins utilized.

Phase II

(1) Develop large pore size, high porosity, ion-conducting membranes, capable of transferring relatively large organic ions such as alkylbenzene sulfonates (ABS).

(2) Determine the fundamental properties of electrodialysis cells constructed with the newly developed high porosity membranes.

(3) Study the best system developed with reference to removal efficiencies for contaminants in actual waste waters and methods for reducing or completely preventing fouling.

2.0 SUMMARY

A novel ion exchange resin in particulate form has been developed which displays an ABS sorptive capacity superior to that of any of the presently available commercial ion exchange resins tested.

Novel ion exchange membranes have been developed which display porosities superior to those of commercially available ion exchange membranes tested. To a limited extent, these novel membranes permit the passage of large organic molecules, such as ABS, under electrodialytic conditions.

Extensive experimentation in the renovation of waste water by means of electrodialysis has shown that:

a) Conventional electrodialysis techniques, employing standard commercial ion exchange membranes, such as those used by Ionics, Inc., in its production electrodialysis stacks, is limited in its effectiveness as a method of waste renovation because of membrane fouling by large organic molecules.

b) Conventional electrodialysis, employing novel, experimental high porosity membranes, is limited in its effectiveness as a method of waste renovation because of excessive electro-osmotic water transfer through these membranes.

c) Modified forms of electrodialysis, such as the electrodeionizer, have demonstrated waste renovation effectiveness superior to that of conventional electrodialysis. This superiority is attributed to the presence of ion exchange beads in the electrodeionizer, which results in increased contact area and lessened electrical resistance. The

effectiveness of the electrodeionizer as a method of waste renovation is limited by the fouling of beads and membranes by large organic molecules.

d) Modified forms of electrodialysis, in which the anion membranes are at least partially protected from organic fouling by the use of protective diaphragms of asbestos, have displayed waste renovation effectiveness superior to that of conventional electrodialysis.

Asbestos has been shown to possess sorptive capacity for organic ions, particularly alkylbenzene sulfonates (ABS.)

The cost of resins and chemical regenerants for the renovation of ABS from secondary sewage by columnar ion exchange would be approximately 1-2 cents per thousand gallons.

The capital cost of an electrodialysis plant to process 10,000,000 gpd of synthetic sewage would be approximately $4,000,000 and the cost per thousand gallons would be about $0.50.

3.0 DEVELOPMENT OF NOVEL ION EXCHANGE RESINS

3.1 Purpose

Ion exchange resins are well established as a means of deionizing aqueous solutions[1]. They can be very effective for the more common inorganic anions and cations. For ionic oil-soluble materials and non-ionic compounds, however, they have only limited utility at present. In particular, generally available ion exchange resins possess a rather fine pore structure which allows them only a limited sorptive capacity. They are also so polar that sorption is primarily the result of ordinary ion exchange, with Van der Waal's forces playing only a minor role. It has been shown that large organic ions, such as ABS, can be removed from water by certain ion exchange resins[2]. It has also been shown that ion exchange capacity can be increased by increasing ion exchange resin porosity[2].

Unfortunately, the ion exchange resins which have been used to sorb ABS were readily fouled by the large organic ion. Regeneration was not easily accomplished and even those resins of the highest available degree of porosity did not display economically attractive capacities.

Novel anion ion exchange resins with pore diameters sufficiently large to accommodate large organic ions, such as ABS, could provide an effective method for removal of refractory materials without the difficulties described above. Properly designed resins of this type should also exhibit high exchange capacities because of large pore size and a high degree of porosity.

3.2 General Procedures Used

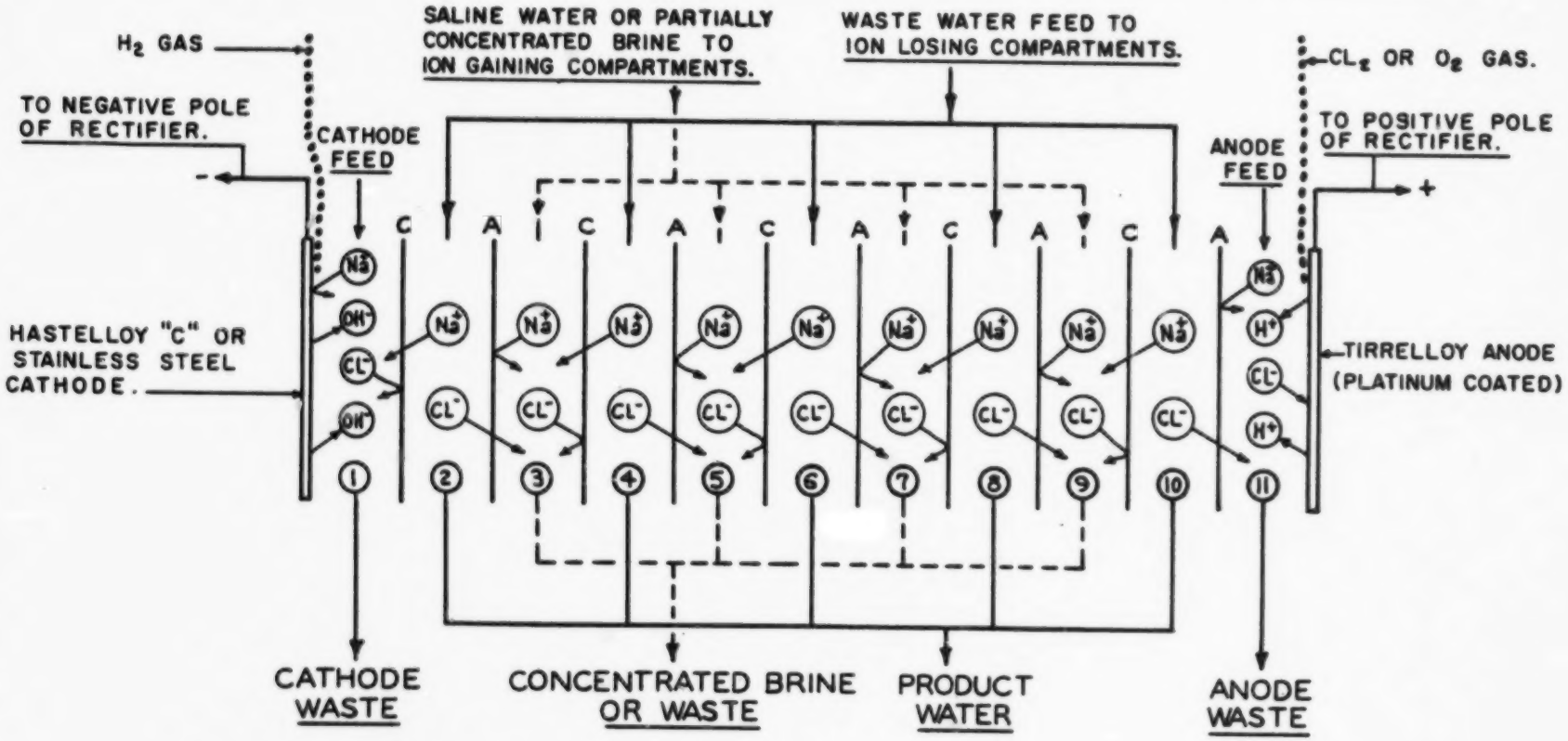
The ion exchange resins discussed above are usually available only in bead form and are particularly adapted to use in ion exchange columns. Electrodialysis, however, requires the use of ion exchange membranes, which perform a somewhat different function from that of ion exchange beads. The ion exchange membranes in an electrodialysis cell serve as ion-permeable hydraulic barriers between liquid streams. The arrangement is usually such that ions are removed from the stream on one side of the membrane, and concentrated in the stream on the other side of the membrane. A simplified diagram of the operation of an electrodialysis cell is shown in Figure 1.

To function properly in an electrodialysis cell, the ion exchange membrane must be mechanically strong and sufficiently porous to permit the passage of the largest ion to be removed from solution.

Our principal goal in both membrane and bead development was, therefore, the same; the development of sufficient porosity to accommodate large organic ions, such as ABS. However, since Ionics' principal experience lies in the field of membrane development, most of our work was directed toward the development of novel ion exchange materials in membrane form. We have found that such ion exchange membranes can be readily converted to particulate or granular form by removal of the membrane backing material from the membrane, followed by mechanical fragmentation of the remaining resin.

FIGURE I.

BASIC ION AND WATER FLOW IN ELECTRIC MEMBRANE STACK.


H_2 GAS
TO NEGATIVE POLE OF RECTIFIER.
CATHODE FEED
HASTELLOY "C" OR STAINLESS STEEL CATHODE.
SALINE WATER OR PARTIALLY CONCENTRATED BRINE TO ION GAINING COMPARTMENTS.
WASTE WATER FEED TO ION LOSING COMPARTMENTS.
CL_2 OR O_2 GAS.
TO POSITIVE POLE OF RECTIFIER.
ANODE FEED
TIRRELLOY ANODE (PLATINUM COATED)
C A C A C A C A C A C A
1 2 3 4 5 6 7 8 9 10 11
CATHODE WASTE
CONCENTRATED BRINE OR WASTE
PRODUCT WATER
ANODE WASTE

LEGEND:

C---CATION MEMBRANE
A---ANION MEMBRANE
(7)--COMPARTMENT NUMBER (SEE TEXT)
(Na^+)--ANY CATION (POSITIVE ION) LIKE SODIUM.
(CL^-)--ANY ANION (NEGATIVE ION) LIKE CHLORIDE.

3.3 Preparation of Novel Ion Exchange Membranes

During the course of our work, we prepared twenty-seven different novel ion exchange membranes which divide naturally into three groups, according to the method of preparation used. The type classifications and formulations of these membranes are described in the tables below:

Group I - Membranes Incorporating Large Molecular Size NP[1] Materials

Membrane No.	% XL[2]	% NP	NP Material	Aminated By
A8	56	70	naphthalene	trimethylamine
A9	56	70	decalin	"
A10	56	90	decalin	"
A11	56	70	dodecylbenzene	"
A12	56	90	dodecylbenzene	"

1 non-polymerizable
2 cross-linking

Group II - Membranes Prepared According to U.S. Patent 2,730,768[1]

Membrane No.	Patent Ex. No.	% XL	% NP	NP Material	Theo. Cl^- Cap.
A13	5	32	29	isopropanol	4.20 meq/gm.
A14	5	31	39	"	5.50
A15	1	22	38	dioxane	5.05
A17	5	27	40	isopropanol	6.07
A18	5	14	36	"	6.74
A19	5	50	50	"	3.38
A20	5	70	70	"	1.60
A21	5	50	50	"	3.56

1. J.T. Clarke - assigned to Ionics, Inc., dated 1/17/56. This invention is concerned with the preparation of synthetic organic polymeric structures of extreme insolubility which are in the form of solvated gels containing active ion exchange groups. Ex.1 treats the copolymer of divinylbenzene and maleic anhydride. Ex.5 treats the copolymer of quaternized 2-vinylpyridine and divinylbenzene.

Group III - Membranes Incorporating Large Molecular Size NP Materials and Aminated with Amines Other than Trimethylamine

Membrane No.	% XL	% NP	NP Material	Amine
A26	56	70	decalin	N,N-diethylethanolamine
A27	"	"	dodecylbenzene	"
A28	"	"	decalin	γ-diethylaminopropylamine
A29	"	"	dodecylbenzene	"
A30	"	"	decalin	γ-dimethylaminopropylamine
A31	"	"	dodecylbenzene	"
A32	"	"	decalin	N,N,N^1,N^1-tetramethyl
A33	"	"	dodecylbenzene	-1,3-butanediamine
A34	"	"	decalin	N,N-dimethylethanolamine
A35	"	"	dodecylbenzene	"
A36	"	"	decalin	triethanolamine
A37	"	"	dodecylbenzene	"
A38	"	"	decalin	triisopropanolamine
A39	"	"	dodecylbenzene	"

All of the membranes described in the three groups above were prepared by Ionics' conventional membrane casting techniques. With few exceptions, the backing or support material used was 4 oz. dynel cloth. Curing cycles used were generally 60-100°C for 48 hours.

3.4 Preparation of Novel Ion Exchange Resin

Only one novel ion exchange resin was prepared in particulate or granular form. This was number A18, the preparation of which is described in Group II above, "Membranes Prepared According to U.S. Patent 2,730,768." Because of its high theoretical capacity, this formulation was selected for reduction from membrane to particulate form. The dynel backing was removed from the membrane by solvent extraction; the remaining resin was then reduced to granules by fragmentation in a Waring Blender.

3.5 Testing the Properties of Novel Ion Exchange Resins

The equilibrium test described by Abrams and Lewon[2] was used to determine the ABS sorptive capacity of our new resins. A known weight of resin was immersed in a known volume of an ABS solution of known concentration until a state of equilibrium was reached between ABS sorbed by the resin and ABS remaining in the solution. The point of equilibrium was determined by periodic analysis of the solution for ABS content, using the methylene blue complex method. ABS capacities have been calculated in terms of milliequivalents of ABS sorbed per gram of dry resin, assuming the equivalent weight of ABS to be 350.

The results of our equilibrium tests with resins in bead or granular form are shown in Table I below. A number of commercial anion ion exchange resins in bead form were tested as controls for our novel experimental resin, A18. The A18 resin was tested in the form of 20-50 mesh granules.

TABLE I

EQUILIBRIUM TEST RESULTS - RESIN IN BEAD FORM

Resin Type	Bead Mesh Size	Conc. ABS mg/l	ABS Cap. meq/gdr.
Dowex 21K	16 - 20	2000	3.9
Dowex 1X8	20 - 50	"	2.6
Dowex 1X8	200 - 400	"	3.5
Dowex 2X8	30 - 50	"	2.6
Dowex 2X8	200 - 400	"	5.2
Exp. A18	20 - 50	"	6.4
Dowex 1X8	200 - 400	10	2.9

A range of mesh sizes was used to determine the effect of surface area upon ABS sorptive capacity. It was noted that the smaller mesh sizes, with their increased ratio of surface area to volume of beads, showed increased ABS sorptive capacity. In the case of the Dowex 2X8 beads, for example, the 200-400 mesh beads demonstrated twice the ABS sorptive capacity of the 20-50 mesh beads.

Experimental resin No. A18 demonstrated the highest ABS sorptive capacity of any of the resins tested; 123% of the nearest standard commercial resin, 200-400 mesh Dowex 2X8. Considering the difference in mesh size between these two resin samples, the advantage enjoyed by the A18 resin is doubtless even greater.

ABS sorptive capacity, as might be expected from theoretical considerations, appears to be a function of the concentration of the ABS solution used for the equilibrium test. Dowex 1X8, 200-400 mesh, for example, showed a capacity of 2.9 meq/gdr when sorbing from a 10 mg/l ABS solution, while it demonstrated a capacity of 3.5 meq/gdr, 20% higher, when sorbing from a 2000 mg/l ABS solution.

The results of equilibrium tests with novel ion exchange resins in membrane form are shown in Table II below. The series of resins A13 through A21 were not equilibrium tested because difficulty was experienced in maintaining these resins in the form of intact membranes. One resin in this series, number A18, was converted to granular form and tested in the bead group (see Table I above). The "standard" membrane in Table II, used as a control, was Ionics' standard commercial anion membrane, designated as AR111-BZL, which employs 4 oz. dynel cloth as backing material.

TABLE II

EQUILIBRIUM TEST RESULTS - RESINS IN MEMBRANE FORM

Membrane	Conc. ABS, mg/l	ABS Cap. meq/gdr
Standard	2000	1.7
Exp. A8	"	2.2
Exp. A9	"	1.7
Exp. A10	"	1.9
Exp. A11	"	2.8
Exp. A12	"	2.5
Exp. A26	1000	0.8
Exp. A27	"	2.1
Exp. A28	"	1.4
Exp. A29	"	0.5
Exp. A30	"	1.0
Exp. A31	"	0.5
Exp. A32	"	0.6
Exp. A33	"	0.7
Exp. A34	"	1.2
Exp. A35	"	1.1
Exp. A36	"	0.4
Exp. A37	"	0.4
Exp. A38	"	negl.
Exp. A39	"	0.5
Standard	100	0.6
Standard	10	0.2

During the course of the equilibrium tests described above, the concentration of the ABS solution used in the tests was reduced from 2000mg/l to 1000 mg/l, which makes direct comparison of all the results difficult. Our analysis of the effect of this change indicates that all results on resins A26 through A39 would have been approximately 20% higher than shown, if these resins had been equilibrated in a 2000 mg/l ABS solution. Resin A27 is the only resin in the A26-A39 series which would surpass the standard if the 20% allowance were made, rising from a value of 2.1 meq/gdr to 2.5 meq/gdr.

Of the nineteen experimental resins tested in membrane form, five showed ABS sorptive capacities superior to that of the standard membrane. The best capacity was demonstrated by No. All, which had a capacity of 165% of the standard membrane, both having been tested at 2000 mg/l ABS concentration.

In the course of the development of novel ion exchange resins described above, we have shown that it is possible to produce ion exchange resins having considerably higher ABS sorptive capacities than presently available materials. This has been achieved by increasing the pore size and degree of porosity of the resins.

No work has been done as yet on the effect of the degree of cross-linking in a resin upon its ABS sorptive capacity.

4.0 ELECTRODIALYSIS STUDIES

Electrodialysis has recognized engineering potential for removal of common inorganic ions from aqueous solution to produce potable water. It is also gaining recognition as a method for demineralizing certain types of organic-containing industrial solutions such as raw sugar and whey. If an electric membrane process could be developed which would be efficient at low electrolyte concentrations and which could effectively remove both inorganic salts and relatively high molecular weight organic ions from sewage effluents, it would be extremely useful for renovation purposes.

It was our purpose to determine the ability of present forms of electrodialysis equipment to renovate sewage and to improve this ability by the development of new equipment and techniques.

Our electrodialysis study began with the use of the simplest possible electrodialysis cell to study the basic behavior of such a cell when used to renovate secondary sewage effluent. The greatest amount of emphasis was placed upon the removal of ABS from solution.

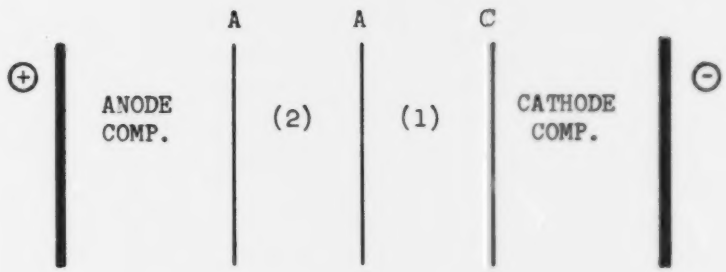
Novel high porosity ion exchange membranes, which have been described previously, were then compared in the simple electrodialysis cell with standard commercial Ionics' anion ion exchange membranes to determine their relative ABS sorptive capacity, their ability to pass ABS, their tendency to permit water transfer, and their properties in general.

Experiments were then conducted in which modifications of the basic electrodialysis cell, such as the electrodeionizer stack, were tried.

Finally, a laboratory bench-scale model of Ionics' commercial electrodialysis stack was employed in tests to determine renovation capacity for both natural secondary sewage effluent and synthetic effluents prepared in the laboratory.

4.1 Experimental Data

A simple electrodialysis cell was designed and built. It was so constructed that the cell components and the spacing between them could easily be changed. A simple schematic drawing is adequate to show the position and relative spacing of the cell components:



The heavy vertical end lines represent the electrodes, anode + and cathode -; the narrow vertical lines represent the ion exchange membranes, A = anion and C = cation, and the numbers designate cell compartments.

If the cell shown above contained sodium and chloride ions in all compartments, the ions would behave as follows when a direct current is applied with the polarity shown:

Na^+ would migrate toward the cathode, passing through the cation membrane and being blocked by the anion membranes; Cl^- would migrate toward the anode, passing through the anion membranes, but being blocked by the cation membrane. Thus, compartment 1 would be freed of both Na^+ and Cl^- and would be said to be "demineralized". If ABS ion were present in solution it would be expected, since it is negatively charged, to behave in the same manner as Cl^-.

When "forward current" is spoken of in electrodialysis, we refer to an arrangement wherein electrical polarity is as shown in the above drawing, with anode positive. When "reverse current" is spoken of, we refer to a situation where the polarity is reversed, with the original anode negatively charged and acting as the cathode.

The current used in our electrodialysis experiments was filtered DC. Electrical arrangements were such that cell voltage and cell current could be continuously monitored.

We were concerned in these experiments with changes in ABS concentration in or between cell compartments. Such changes were determined by sampling and analyzing the sample for ABS. A number of experimental runs were made with the basic electrodialysis cell just described. The purpose of each of these runs and the results obtained are discussed below.

Will ABS pass through a standard Ionics' anion membrane under electrodialytic conditions?

The physical arrangement of the cell used was that described above. The membranes used in the cell were Ionics' standard production 4 oz. dynel-backed anion and cation membranes. All cell compartments were filled with a 100 mg/l ABS solution, prepared with a standard alkylbenzene sulfonate sample containing 54.8% ABS and 40.3% Na_2SO_4*.

Voltage (14V) was applied to the cell and it was found that the cell current gradually declined. It was found that the ABS concentration in compartment 1 had fallen during the course of the run from 100 mg/l to 3.5 mg/l, indicating that ABS might have migrated from compartment 1 into compartment 2, through the anion membrane between these two compartments. When reverse current was applied, we naturally expected to find that the ABS concentration in compartment 1 had returned to the original 100 mg/l; this was not the case, however, the ABS concentration in compartment 1 remaining at 3.5 mg/l.

We theorized from these results that the ABS had either:

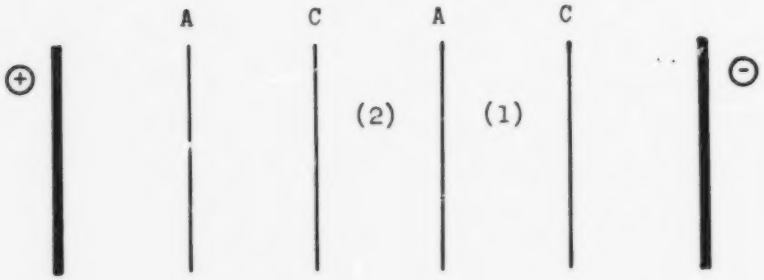
1. been trapped in the anion membrane;
2. formed a film upon the surface of the anion membrane;
3. passed through the anion membrane into compartment 2 and, for some reason, had been unable to return under reverse current.

---

* Standard alkylbenzene sulfonate, lot 3, June 1961, Association of American Soap and Glycerine Products, Inc., 295 Madison Avenue, New York 17, N.Y.

A repeat run, made with vigorous stirring of compartment 1 to eliminate the formation of any surface film of ABS upon the anion membrane, yielded results substantially identical to those of the original run. Increasing the cell voltage applied during the reverse current cycle from 14V to 60V did not cause the ABS concentration in compartment 1 to rise.

In order to eliminate the possibility of ABS having passed through both the anion membranes between it and the anode and having been destroyed at the anode, we arranged a "trap" for the ABS as shown in the cell schematic diagram below:

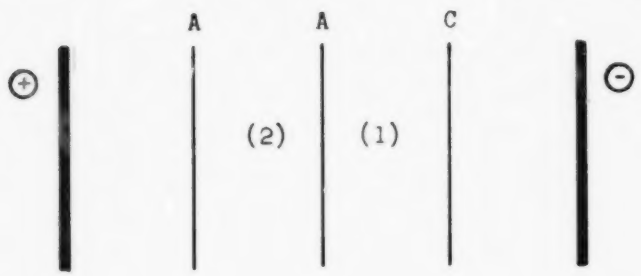


Compartment 2 formed a "concentration cell" into which an anion from compartment 1 could pass with the polarity as shown, but where it would be trapped because of the cation membrane interposed between it and the anode. Compartment 1 was filled with 100 mg/l ABS solution, while all other compartments were filled with 400 mg/l NaCl. The application of forward current lowered the ABS concentration in compartment 1 from 100 mg/l to 20 mg/l. The ABS concentration in compartment 2 remained at 0 mg/l. Application of reverse current did not result in any increase in the ABS concentration in compartment 1.

These results made it obvious that ABS was being trapped in the anion membrane and was not passing through it or forming a film upon its surface.

Is there a threshold concentration of ABS within the membrane above which ABS might be withdrawn by reverse current?

The next cell run was made with the simple cell arrangement shown below:



Our objective here was to saturate the anion membrane between compartments 1 and 2 as completely as possible with ABS and then determine if reverse current would withdraw any ABS from the membrane. It was planned to recognize the saturation point of the membrane by noting that point at which the cell current dropped to a minimum and could not be raised further by additions of salt to compartment 1. 10,000 mg/l ABS solution was placed in compartment 1 and additions were made as required during the period of application of forward current. When the point of no further current rise was noted (membrane saturation) polarity was reversed. No ABS was withdrawn from the membrane by the current reversal, based on analysis of compartment 1.

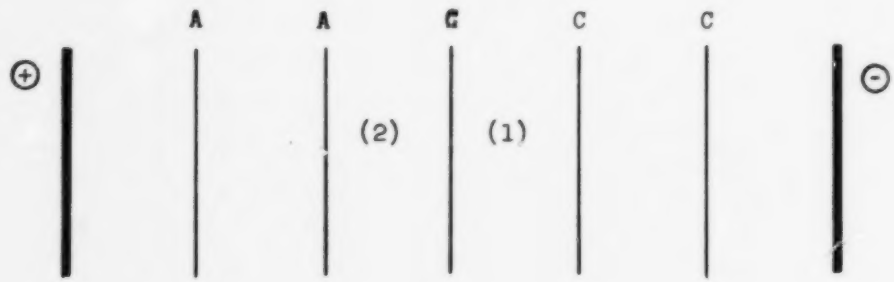
The saturated anion membrane was withdrawn from the cell and the ABS eluted from it, employing the elutive solution developed by Abrams and Lewon[2], which consists of a 50/50 mixture by volume, of 1N hydrochloric acid and acetone. A large amount of ABS was removed from the membrane by this elution. There was no apparent damage to the membrane.

These results indicated that the anion membrane can be saturated with ABS under electrodialytic conditions but will not desorb the ABS under the influence of reverse current.

Will a cation membrane sorb ABS as an anion membrane does?

We have assumed that the sorption of ABS by an anion ion exchange membrane was due to the charged nature of the membrane. It was necessary to determine whether a cation ion exchange membrane, charged opposite to the anion membrane, would sorb ABS under electrodialytic conditions.

A simple test cell was set up as shown:



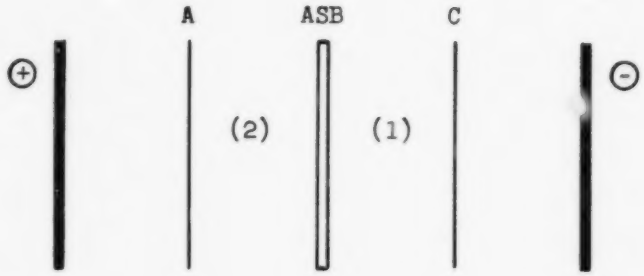
Compartment 1 was filled with 10,000 mg/l ABS solution. All other compartments were filled with 400 mg/l NaCl solution. There was no detectable loss of ABS from compartment 1 under forward current. From this result we could only conclude that the charge on the membrane determines whether or not it will sorb ABS.

Increasing the useful sorbing life of anion ion exchange membranes

It appeared to us that an ABS-retentive diaphragm placed close to or in contact with the anion membrane might have beneficial results in prolonging the useful life of the membrane. The ABS ions would be forced to enter the retentive diaphragm because of the attraction of the anode; if they could be retained within the diaphragm they would not be able to enter and foul the membrane, while at the same time inorganic ions would be able to pass through both the diaphragm and the membrane. If a high concentration of ABS could be developed within the retentive diaphragm, the diaphragm could then be removed from the cell, discarded

and replaced by a fresh diaphragm. Even better, it might be possible to remove the ABS load from the diaphragm in situ by the application of reverse current.

A material suggested for such a diaphragm was asbestos. The cell configuration shown below was set up and used to test the ABS sorptive ability of an asbestos diaphragm. The asbestos used was Carey 1-30, acid bond, .028" thick:



ASB = Asbestos Diaphragm

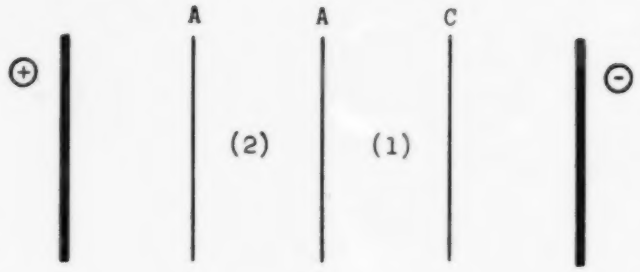
Compartment 1 was filled with 10,000 mg/l ABS solution. All other compartments were filled with 400 mg/l NaCl solution. After application of forward current for one hour, it was found that the ABS concentration in compartment 1 had dropped from 10,000 mg/l to 6000 mg/l and the ABS concentration in compartment 2 had risen from 0 to 244 mg/l.

Considering the relative volume of compartments 1 and 2 (compartment 1 had 1.5 times the volume of compartment 2) it was obvious that a large proportion of the ABS lost from compartment 1 had been trapped within the asbestos diaphragm, since the ABS concentration in compartment 2 did not rise in proportion to the loss from compartment 1.

Will ABS sorption by the anion membrane take place at low ABS concentrations?

The preceding electrodialysis cell runs were made with ABS solutions in the 100 to 10,000 mg/l range. It was important to determine whether conclusions previously drawn would be valid when ABS solutions of low concentration, say

10-100 mg/l ABS, were used. The following cell set-up was used in this experiment:



Compartment 1 was filled with 90 mg/l ABS solution, all other compartments with 400 mg/l NaCl solution. After one hour or forward current operation, the ABS concentration in compartment 1 had fallen to 7 mg/l while compartment 2 showed less than 1 mg/l ABS.

The run described above was then repeated, this time using a 10 mg/l ABS solution in compartment 1. After one-half hour of forward current, the ABS concentration in compartment 1 had fallen to 2.7 mg/l while the ABS concentration in compartment 2 was found to be less than 1 mg/l.

These two runs demonstrated that the anion membrane would sorb ABS under electrodialytic conditions from ABS solutions as low in concentration as 10 mg/l.

Saturation of an anion membrane with ABS

This experiment was made to get quantitative data concerning the amount of ABS which an anion membrane could sorb under electrodialytic conditions. A simple test cell was set up as in the preceding experiment. An 18 liter reservoir was provided, from which a 40 mg/l ABS solution was pumped through compartment 1 at the rate of 500 ml/min. This was done to provide the membrane with a constantly replenished supply of ABS to sorb. NaCl was added to the 18 liter

reservoir as needed to make up for the deionization occurring in compartment 1. Cell current was held at 0.9 ampere, producing a current density of 12 amperes per square foot of membrane area. The electrode products in the electrode compartments were removed periodically and replaced with fresh 400 mg/l NaCl solution.

The cell was operated under forward current for 56 hours. After this period of time the ABS concentration in the 18 liter reservoir had fallen from 40 mg/l to 4.3 mg/l. At this point the run was discontinued because it was obvious that the rate of ABS sorption by the anion membrane was asymptotic and that an unduly long period of operation would be required to reduce the ABS concentration of the reservoir to zero. At the end of the run only 3.5 mg/l ABS were found in compartment 2, indicating only the very slightest transfer of ABS ions through the membrane.

The cell was then drained. All compartments were filled with 400 mg/l NaCl solution and reverse current was applied for 2-1/2 hours. Analysis of compartment 1 then showed only 3.8 mg/l ABS, indicating only a very minor reverse current withdrawal of ABS from the anion membrane.

During the run the anion membrane was found to have sorbed 0.163 meq of ABS per square inch. We had previously determined by means of equilibrium tests, that a one-inch square of standard anion membrane, sorbing from <u>two</u> sides from 100 mg/l ABS solution, would sorb 0.14 meq of ABS or 0.07 meq/in^2 of exposed surface. In this run, where the membrane was sorbing from one side only, we have found a much higher ABS sorptive capacity than that encountered under equilibrium conditions.

A special equilibrium run was made at this point to determine whether ABS sorption by the anion membrane was purely a surface effect. One-inch squares were cut from chemically identical anion ion exchange membranes, one of which was three times as thick as the other. These two squares were equilibrated in 2000 mg/l ABS solution. The thin sample sorbed 0.385 meq of ABS, the thick sample 0.394 meq of ABS. This showed that the amount of ABS sorbed was a function of exposed <u>area</u>, not volume.

While we did not reach complete saturation of the anion membrane in the electrodialysis experiment just described, it was shown that the anion membrane would sorb ABS from a solution as low in concentration as 4.3 mg/l ABS and that the rate of sorption declines with decreasing ABS concentration. This run also substantiated our previous conclusion that ABS is sorbed irreversibly by the membrane.

To determine the ultimate ABS sorptive capacity of the anion membrane

This experiment was designed to provide the sorbing membrane with a constant rich supply of ABS to sorb so that its ultimate capacity could be determined. The cell arrangement was the same as in the preceding experiment. No reservoir or pumping was used. Compartment 1 was filled with 10,000 mg/l ABS solution and all other compartments were filled with 400 mg/l NaCl solution. Whenever the ABS concentration of compartment 1 fell appreciably during the course of the run, its contents were removed and replaced with fresh 10,000 mg/l ABS solution. All withdrawals were saved and used to strike a material balance at the end of the run.

After 11-1/2 hours of forward current operation, this run was terminated because the sorbing membrane was found to be badly bulged and puckered on the compartment 1 or sorbing side. The membrane was also found to contain several pinholes, although it had been examined and found to be sound at the beginning of this run.

The twelve square inches of membrane exposed to the ABS solution were found to have sorbed 0.5 meq of ABS per square inch. In view of the condition of the membrane at the end of this run, we must conclude that 0.5 meq of ABS sorbed per square inch of membrane surface is well past the danger point for membranes and should never be approached in any practical application of electrodialysis to ABS sorption.

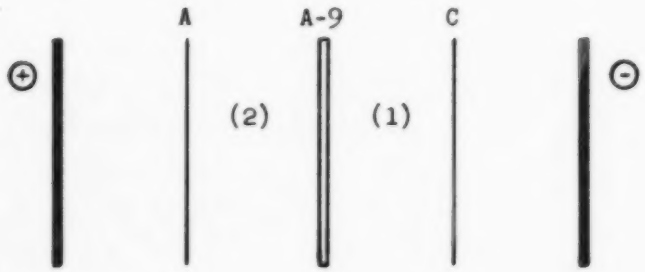
When the bulging, puckered, ABS saturated membrane was eluted to remove the ABS from it, it regained its previous smooth, planar form and, except for the pinholes previously mentioned, appeared to be undamaged.

The bulging of the membrane may be attributed to the sorption of ABS on one side only, resulting in a swelling of that side due to pressure within the membrane pores.

Testing the properties of novel ion exchange membranes in the electrodialysis cell

Experimental membranes A9 and A11 were selected from the group of newly developed membranes to be tested in the electrodialysis cell. These two membranes were chosen because both had displayed good ABS sorptive capacities and both were mechanically strong and thus capable of being tested in an electrodialysis cell.

Experimental membrane No. A9 was a high porosity membrane made with 70% decalin as non-polymerizable material. It was tested in a simple electrodialysis cell of the configuration shown below:



Compartment 1 was filled with 1000 mg/l ABS solution and all other compartments with 400 mg/l NaCl solution. After 19 hours of forward current, the concentration of ABS in compartment 1 had fallen from 1000 mg/l to 4.6 mg/l. Reverse current did not remove any appreciable amount of ABS from this porous membrane. We did observe, however, considerable water transfer through the

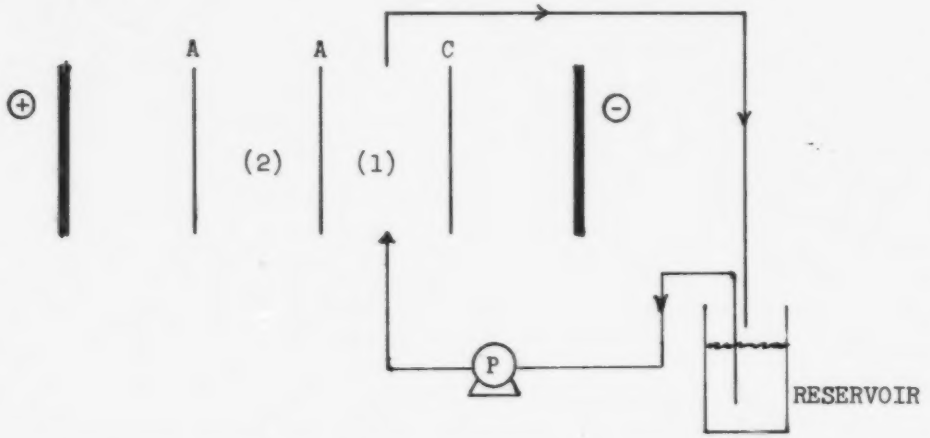
membrane during the forward current cycle, the flow of water being from compartment 1 into compartment 2, in the direction of current flow. This water transfer phenomenon is common in electrodialysis and is called electro-osmosis, which may be defined as "the migration of a liquid past a solid surface under the influence of an external e.m.f." In this particular case, the water transfer through the membrane is disadvantageous, since water from which ABS has been removed is carried out of the renovating compartment.

The experiment indicated that experimental membrane No. A9 sorbed ABS in the same manner as the standard anion membrane with the exception of the high rate of water transfer through it. We now set out to determine its ultimate capacity for ABS, using the same procedure previously used for this purpose with the standard membrane. The experimental membrane was exposed to a 10,000 mg/l solution of ABS from which to sorb, the ABS solution being replenished as needed. After 16 hours of forward current operation, the experimental membrane was found to have sorbed 0.5 meq/in^2, the same amount which was sorbed by the standard membrane under nearly identical conditions. The membrane was slightly bulged toward the sorbing side but returned to its original flat condition when eluted. There was some ABS transfer through this highly porous membrane; 46 mg/l ABS were found in compartment 2, by far the greatest ABS transfer noted up to this point.

Experiment membrane No. All was then tested in the same manner as membrane A9. All was a high porosity membrane prepared with 70% dodecylbenzene as non-polymerizable material. When subjected to 13 hours of forward current electrodialysis in contact with a 10,000 mg/l solution of ABS, it sorbed only 0.11 meq/in^2, far less than the 0.5 meq/in^2 sorbed by the standard membrane and experimental membrane A9 under similar conditions. The reason for this deficiency is unknown at the present time. There was some ABS transfer through the All membrane (10 mg/l) but not nearly as much as that encountered with membrane A9 (46 mg/l).

Saturating a standard anion membrane with ABS from a 10 mg/l solution

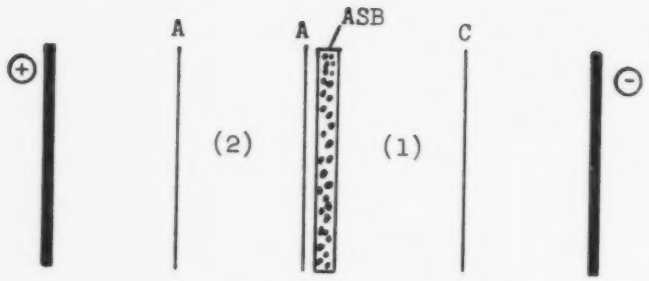
This electrodialysis run was made to simulate, at least partially, the conditions which might be encountered in actual practice, where very low ABS concentrations are encountered. A cell arrangement as shown below was used:



The reservoir contained 18 liters of 10 mg/l ABS solution and it was calculated from previous data that the standard anion membrane used would sorb 4.7 meq of ABS. After 140 hours of forward current operation, when the rate of ABS sorption approached zero, 4.3 meq of ABS, or 92% of the calculated capacity were found to have been taken up. Very little transfer of ABS to compartment 2 occurred.

The protective action of asbestos against membrane "fouling"

It was the purpose of this experiment to determine the protective effect of an asbestos diaphragm placed against the sorbing side of a standard anion membrane in an electrodialysis cell. The cell set-up used was as shown:



A = Anion Membrane
C = Cation Membrane
ASB = Asbestos Diaphragm
0.1 in. thick

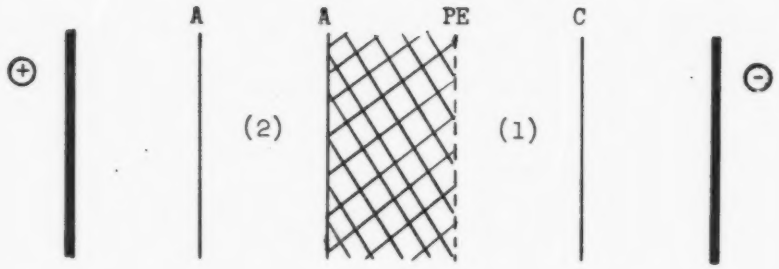
Compartment 1 was filled with 1000 mg/l ABS solution, all other compartments with 400 mg/l NaCl solution. Forward current caused the concentration of ABS in compartment 1 to drop from 1000 mg/l to 250 mg/l. The cell was then disassembled and the anion membrane and asbestos diaphragm tested for ABS content. The results:

1.	ABS found in membrane, by elution with acetone - HCl	24%	
2.	ABS found in diaphragm, by water wash	49%	76%
3.	ABS found in diaphragm, by elution following water wash	27%	
		100%	

The percentages used above refer to the percent of ABS which was lost from compartment 1 during the electrodialysis. These figures show that the asbestos diaphragm did partially protect the membrane from ABS sorption (or "fouling"), allowing only 24% of the ABS to penetrate the protective layer and enter the membrane.

The electrical desorption of ABS from asbestos

For this experiment, a cell similar to that used in the preceding experiment was prepared. The asbestos layer was made much thicker this time and was contained on one side by a microporous polyethylene diaphragm, as shown in the drawing below:



A = anion membrane

C = cation membrane

PE = microporous polyethylene diaphragm

= asbestos fiber, Carey I-30

Compartment 1 was filled with 93 mg/l ABS solution, all other compartments with 100 mg/l NaCl solution. After 90 minutes of forward current, the ABS concentration in compartment 1 had been reduced from 93 mg/l to 38 mg/l. 82 minutes of reverse current brought the concentration of ABS in compartment 1 up from 38 mg/l to 69 mg/l.

It is evident from these results that ABS can be desorbed from asbestos upon which it has been sorbed, at least up to 74% recovery. The electrical regeneration of asbestos should be investigated further in any extension of the present contract because of the practical significance of the above results.

It has been shown that anion membranes become fouled with ABS during electrodialysis. It may be assumed that other relatively large organic ions found in sewage effluents will cause similar fouling. If a cheap material such as asbestos ($40+ per ton, depending upon fiber grade) can be incorporated in an electrodialysis stack, or even used as a prefilter, in such a manner that the fouling of the anion membranes is prevented or considerably delayed, a significant improvement in performance may be realized. The use of electrodialysis stacks which incorporate asbestos protective diaphragms is described later in this report, as is experimental work on the sorptive properties of asbestos.

4.2 The Electrodeionizer Stack

The electrodeionizer stack is an electrodialysis device which is more sophisticated in concept than the simple electrodialysis cell previously used. The basic difference is the packing of the spaces between membranes with ion exchange beads. These beads not only function as ion exchangers themselves, they also serve to provide a highly conductive path between membranes, thus lessening overall cell resistance. Such a stack is shown in Figure 2.

When the sewage effluent, or other solution to be demineralized, enters the stack, it flows through channels formed by anion and cation ion exchange membranes. These channels are filled with ion exchange beads which form a conductive bridge between membranes, as well as providing large contact area and promoting turbulent flow. In our experiments anion ion exchange beads were used to pack the stack although, of course, mixtures of anion and cation beads could have been used, with a resulting lowering of stack resistance. However, the cation ion exchange beads would have made no contribution toward ABS removal.

In the first trial run with an electrodeionizer stack, Leominster sewage effluent[3] was run through the stack in a single pass at the rate of 100 ml/minute, applying 30V to the stack electrodes. The results were as shown:

Refractory	Input	Output	% Renovation
ABS, mg/l	4.2	0.7	83
COD, mg/l	21	< 3	86
Cl^-, mg/l	52	21	60

The results of this first trial were encouraging, particularly in respect to the renovation of ABS and COD. Therefore, further renovation runs were planned in which voltage, flow rates and input concentrations would be varied.

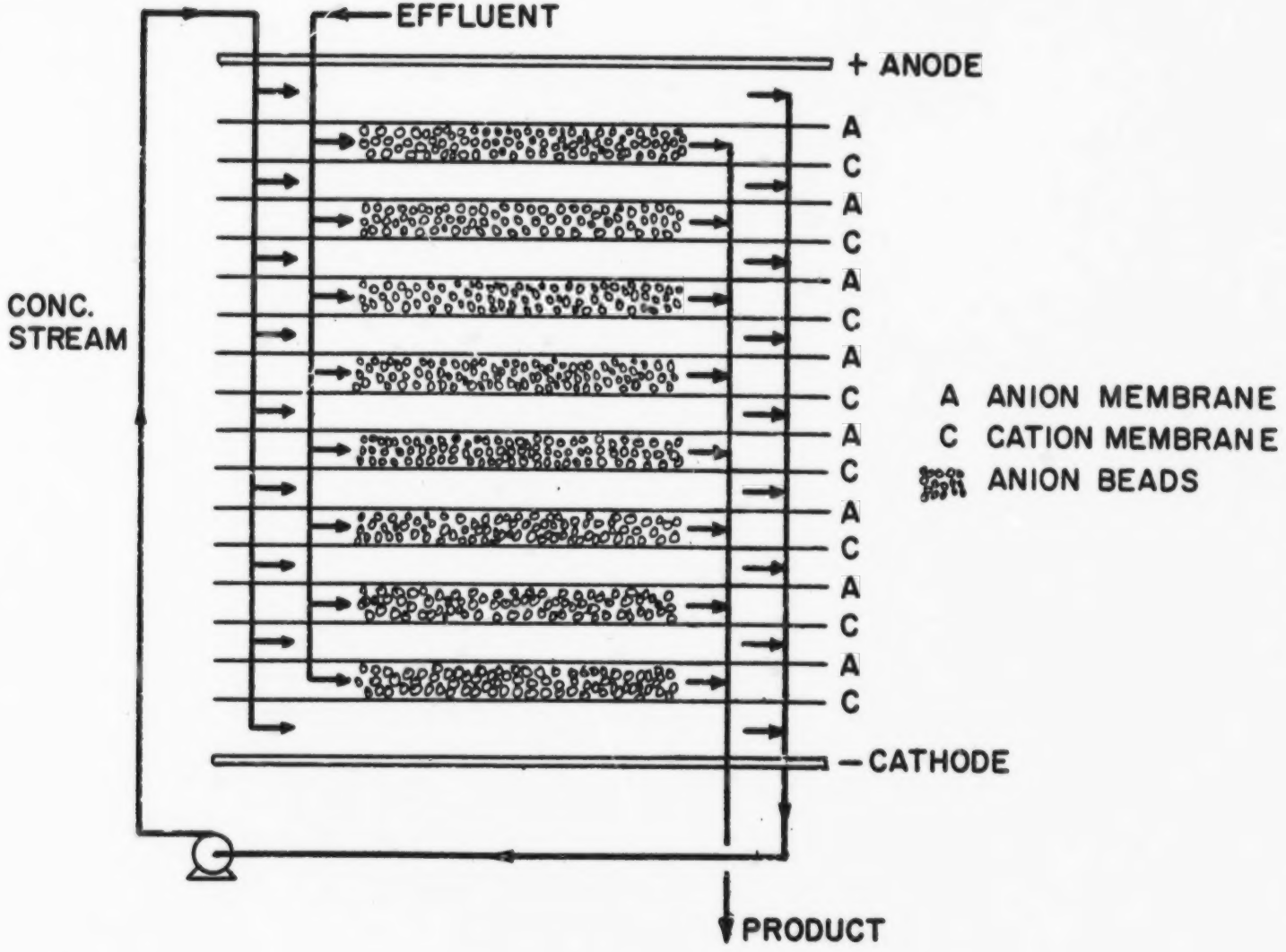


FIGURE 2
ELECTRODEIONIZER STACK

A series of test runs was made with the electrodeionizer stack to determine the effect of applied voltage upon stack performance. The test conditions and the results obtained are shown below:

(1) No voltage applied:

Refractory	Input	Output	% Renovation
COD, mg/l	45.0	32	29
ABS, mg/l	4.2	0.8	81
Cl^-, mg/l	21.0	98	--

(2) 15 volts applied:

Refractory	Input	Output	% Renovation
COD, mg/l	45.0	27	40
ABS, mg/l	4.2	0.6	86
Cl^-, mg/l	21.0	1.4	93

(3) 30 volts applied:

Refractory	Input	Output	% Renovation
COD, mg/l	45.0	26	42
ABS, mg/l	4.2	0.6	86
Cl^-, mg/l	21.0	3.5	83

Conclusions which can be drawn from these runs are:

a) The electrodeionizer stack will sorb ABS and COD even when no voltage is applied, due to the sorbing action of the beads.

b) Some current flow is evidently necessary to get Cl^- removal. The rise in Cl^- level in the no-voltage run was probably due to displacement of Cl^- from the chloride form anion beads by ABS and COD and might serve as a measure of the ABS-COD removed.

c) Doubling stack voltage from 15 to 30 volts did not result in improved renovation. The optimum operating voltage of this stack was not determined but probably lies near 15 volts and depends upon a number of factors, principally liquid flow rates, concentrations of the input stream, and membrane spacing. Excessive voltage and resulting excessive current may cause polarization which decreases stack efficiency.

No TDS or conductance determinations were made during the course of any of these or succeeding runs discussed in this report. Further experiments with the electrodeionizer stack are described under "Combined Methods of Renovation" later in this report.

4.3 The Laboratory-Scale Electrodialysis Stack

The laboratory-scale electrodialysis stack is a scaled-down version of the standard Ionics' commercial demineralizing stack. Its construction is similar to that shown in Figure 1. The lab. stack has approximately 1/2% of the capacity of Ionics' Mark III stack, Ionics' largest stack.

The inter-membrane spaces in the laboratory stack, which employs 9" x 10" membranes, are filled with plastic spacers designed to promote turbulent flow of the incoming liquid stream across the surface of the membranes. The membranes used were Ionics' commercial 4 oz. dynel-backed anion and cation types, and the stack was assembled as an 8 cell-pair unit.

Before attempting to renovate sewage effluent with this stack, it was tested with a salt solution as input to be sure that there were no leaks and that it was in proper operating condition. Two tests were made, under different conditions, as shown:

Test No.	Volts	Ma.	Conc. Flow ml/min	Dil. Flow ml/min	Cl^-, mg/l Input	Cl^-, mg/l Output	% Change
1	80	90	42	19	309	35	89
2	80	125	360	33	309	58	81

These results indicated that the stack was in good working order.

Secondary sewage effluent obtained from the City of Leominster was passed through the stack under the following conditions and with the results shown:

		Refractory	Input	Output	% Renovation
Volts:	80				
Ma.:	110	COD, mg/l	45	14.7	67
Conc. Flow:	190 ml/min	ABS, mg/l	4.2	1.25	70
Dil. Flow:	93 ml/min	Cl^-, mg/l	21	2.8	87

The renovation accomplished here with this relatively mild effluent was sufficiently good to warrant a trial with the much more refractory synthetic sewage 6568[5]. The conditions used and results obtained were as shown:

		Refractory	Input	Output	% Renovation
Volts:	80				
Ma.:	100	COD, mg/l	117	54.0	54
Conc. Flow:	160 ml/min	ABS, mg/l	10	2.7	73
Dil. Flow:	42 ml/min	Cl^-, mg/l	212	17.7	92

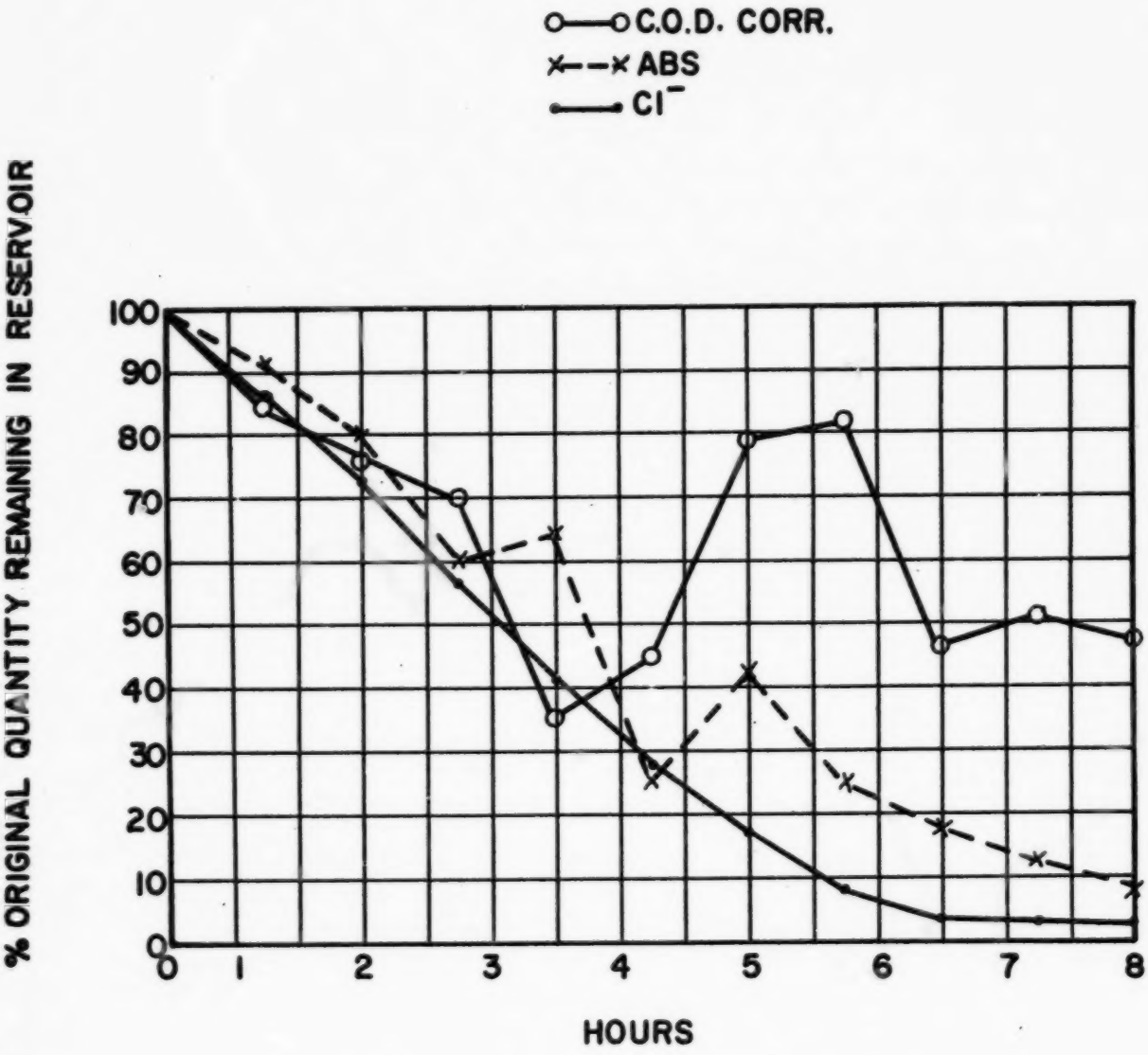
The renovation here, considering the higher input concentrations, was considered to be very promising. We decided to go ahead and determine the capacity or "staying power" of the stack, fearing that eventually the stack membranes would become fouled with ABS and COD and thus lose their effectiveness.

Eight successive 2-liter increments of synthetic sewage 6568 were passed through the stack in an attempt to foul it and destroy its power to renovate sewage. The conditions used were: volts 85; ma. 130; conc. flow 400 ml/min and dilute flow 51-63 ml/min. The table below shows the results obtained with each of the eight renovation runs:

		Output of Run No.							
Refractory	Input	1	2	3	4	5	6	7	8
COD, mg/l	134	77	76	89	93	86	87	96	85
ABS, mg/l	9.8	9.8	2.9	4.7	4.8	3.8	3.2	4.1	3.5
Cl^-, mg/l	220	64	71	78	65	51	53	51	44

FIG. 3

LAB. ELECTRODIALYTIC STACK VS. SYN. SEWAGE 6568



After this series of runs it was obvious that the stack was not going to lose its effectiveness quickly.

A recirculating system was set up to pump synthetic sewage 6568 through the stack and back into an 18 liter reservoir, at a flow rate of 400 ml/min. Samples were taken periodically from the reservoir to observe the course of the renovation. The results are plotted in Figure 3 in terms of "percent of original concentration remaining in reservoir" vs. time. The input reservoir was not well agitated during this experiment which may account for the hump in the COD curve.

The above run was repeated with good agitation of the input reservoir and with increased flow rates; input flow rate 510 ml/min (8.1 gph) and concentrate stream flow rate 570 ml/min (9.05 gph). The results of this recirculating run are shown graphically in Figure 4. Note that there is no hump in the graph, as there was in the preceding run, although there are some unexplained irregularities in the early part of the COD and ABS curves. ABS reduction is not as good in the second run as in the first. Whether this indicates that the cell membranes are becoming ABS-saturated is not yet apparent.

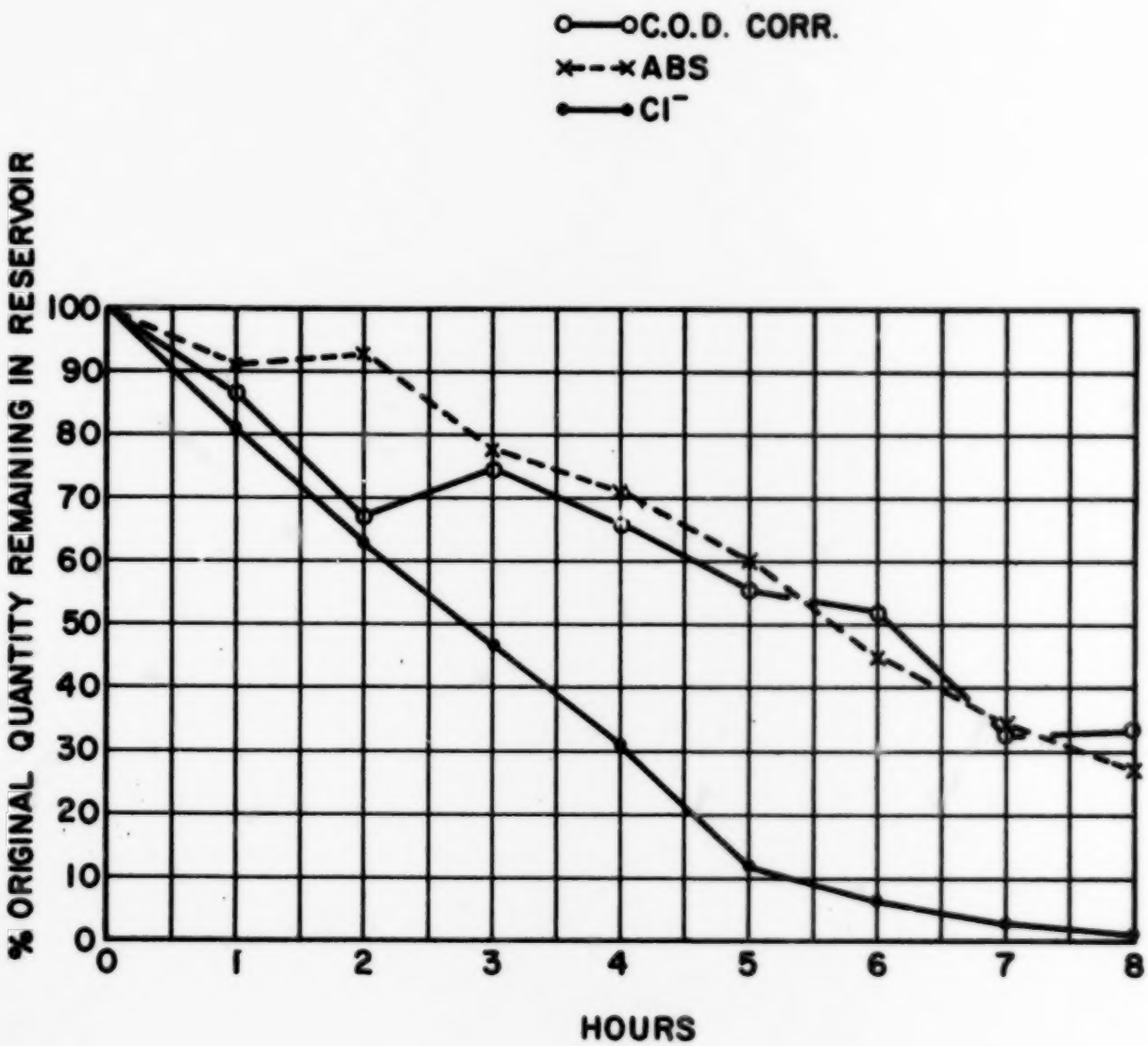
Laboratory Stack with Asbestos Protective Diaphragms

Having shown, (1) that the lab. stack would renovate a refractory sewage, and (2) would continue to do so through a series of runs, protective asbestos diaphragms were incorporated in the stack to determine the effect that such diaphragms might have on its performance. Asbestos sheets (Carey I-30, acid bond, 0.027" thick) 6-1/2" square were inserted in the stack, placing them directly in contact with the input stream side of each anion membrane.

With this arrangement all of the anions in the input stream would be forced to flow through the asbestos diaphragms before contacting the anion membranes. It was hoped that COD and ABS would be trapped within the asbestos sheets and thus be prevented from fouling the anion membranes. Inorganic ions

FIG. 4

LAB ELECTRODIALYTIC STACK VS SYN. SEWAGE 6568



were expected to pass through the asbestos freely and then on into and through the anion membranes.

A series of runs was made with the asbestos shielded stack. The input solution used was synthetic sewage 6568. Both the dilute and concentrate streams were recirculated through the stack by pumping from individual reservoirs. The dilute stream reservoir was monitored periodically for ABS, COD and Cl^- content to determine the progress of the renovation. The purpose and the results of each of the runs in this series are shown below:

1) Trial run to test stack

Time, hrs.	Volts	Ma.	ABS	COD	Cl^-	
0	30	350	9.2	126	232	Dil. Flow: 660 ml/min
1/4	"	165	7.1	108	184	Conc. Flow:185 ml/min
1/2	"	110	6.2	97	106	Conc. Sol: 1000 mg/l NaCl
1	"	62	2.8	64	40	
1-1/2	"	44	2.3	56	28	
2	"	30	1.7	50	26	
2-1/2	"	25	1.7	50	25	
% Ren.	-	-	81	60	89	Total Passes: 25.5

This run was encouraging because a good percentage of each of the three refractories was removed. The item "passes", used above, indicates the number of times that the contents of the one gallon input reservoir passed through the stack during the 2-1/2 hour run.

2) Attempt to keep current constant during run, by varying voltage

Time, hrs.	Volts	Ma.	ABS	COD	Cl^-	
0	30	350	11.7	124	230	Dil. Flow: 660 ml/min
1/4	30	140	10.6	104	162	Conc. Flow: 185 ml/min
1/2	40	125	10.6	89	114	Conc. Sol: 1000 mg/l NaCl
1	50	82	8.6	63	50	
1-1/2	60	65	8.4	48	22	
2	70	53	2.4	47	24	
2-1/2	80	54	1.9	42	20	
% Ren.	--	--	84	66	91	Total Passes: 25.5

Renovation was good here also, a little better than the preceding run.

3) Attempt to keep current constant by addition of salt to the dilute (input) solution during the course of the run

Time, hrs.	Volts	Ma.	ABS	COD	Cl^-	
0	30	220	9.2	126	232	Dil. Flow: 660 ml/min
1/4	"	150	8.2	116	196	Conc. Flow: 185 ml/min
1/2	"	170	8.0	108	252	Conc. Sol: 1000 mg/l NaCl
1	"	155	5.9	94	224	
1-1/2	"	175	4.0	91	272	
2	"	165	4.2	106	256	
2-1/2	"	170	3.9	74	278	
% Ren.	-	-	58	41	-	Passes: 25.5

Although we succeeded in keeping current fairly constant during the course of this run, it was not an efficient run. It was felt that the stack membranes might be becoming saturated (fouled).

4) To check stack after preceding run to see if it is still functioning properly

Time, hrs.	Volts	Ma.	ABS	COD	Cl^-	
0	30	185	9.2	126	232	Dil. Flow: 660 ml/min
1/4	"	130	8.2	109	174	Conc. Flow: 185 ml/min
1/2	"	105	7.2	96	134	Conc. Sol: 100 mg/l NaCl
1	"	74	4.9	94	80	
1-1/2	"	53	5.4	68	54	
2	"	42	3.1	81	34	
2-1/2	"	34	2.9	65	22	
% Ren.	-	--	68	48	90	Passes: 25.5

The results of this run are very similar to the first run of the series, which indicates that the stack is still in good operating condition and the membranes are not fouled. At the conclusion of this run we analyzed the concentrate solution and found that it contained 0.98 mg/l ABS.

5) Repeat of Run No. 4 to check stack performance

This run was a duplicate of Run No. 4 above and was made to see if the saturation point of the stack was being approached. Results were very much the same as in Run No. 4. 0.75 mg/l of ABS was found in the concentrate stream reservoir. We decided after this run to attempt a reverse current regeneration of the stack.

6) Regeneration of stack by current reversal

The dilute side of the stack was first rinsed thoroughly by pumping tap water through it with no current applied.

A 2-liter reservoir of tap water was recirculated through the dilute side and a 2-liter reservoir of 100 mg/l NaCl solution was recirculated through the concentrate side. Current was then applied to the stack in the reverse direction (anode negative).

Time, min	Volts	Ma.	Remarks
0	30	700	
10	30	600	
16	30	1000	Raise voltage to increase current
33	50	750	Add 100 ml 40 g/l NaCl to Conc.Reservoir
36	50	1500	
44	50	1450	
48	50	750	Shut Down

If the regeneration succeeded, ABS should have appeared in quantity in the dilute reservoir; it did not, only 1.1 mg/l of ABS was found at the end of the run, although the salt content of the dilute reservoir rose from 0 to 745 mg/l. This ABS recovery, of course, represents only a very small part of the ABS sorbed by the stack during the course of the five runs which preceded the regeneration run.

7) Renovation run, to determine the effect upon the stack of the attempted regeneration (#6 above) and to check the effect of using a slower dilute stream flow

The dilute stream flow rate was dropped from the previously used 660 ml/min to 260 ml/min in this run, a 60% reduction.

Time, hrs.	Volts	Ma.	ABS	COD	Cl^-	
0	30	470	10	125	231	Dil. Flow: 260 ml/min
2-1/2	30	59	3.3	61	32	Conc. Flow: 185 ml/min
% Ren.	--	--	67	51	86	Conc. Sol: 1000 mg/l NaCl

ABS found in Conc. Reservoir: 0.82 mg/l Passes: 10

This renovation run was just about as effective as its predecessor, No. 4. The attempted regeneration evidently has little effect upon stack performance. The slower input flow rate did not affect the renovation materially.

8) Renovation run, increased dilute stream flow rate

In this run the dilute stream (input) flow rate was increased from 660 ml/min to 1090 ml/min, an increase of 65%.

Time, hrs.	Volts	Ma.	ABS	COD	Cl^-		
0	30	360	10	125	231	Dil. Flow:	1090 ml/min
2-1/2	30	36	1.9	17	28	Conc. Flow:	185 ml/min
% Ren.	--	--	81	86	88	Conc. Sol:	1000 mg/l NaCl

ABS found in Conc. Reservoir: 0.9 mg/l. Passes: 42

This was our most effective renovation run. It must be kept in mind, however, that the input solution made 17 more passes through the stack than it did when running at the slower flow rate previously used, 660 ml/min.

9) Recapitulation of seven renovation runs with lab stack

Run No.	% of Refractories Ren. in 2.5 hours			Dil. Flow ml/min	No. of Passes
	ABS	COD	Cl^-		
1	81	60	89	660	25.5
2	84	66	91	660	25.5
3	58	41	--	660	25.5
4	68	48	90	660	25.5
7	67	51	86	260	10
8	81	86	88	1090	42

10) Renovation run, non-recirculated

Using the same lab stack, we pumped an 18-liter reservoir of synthetic sewage through the stack and collected the output in a separate reservoir where it was analyzed. The dilute flow rate was 1000 ml/min (15.8 gph), the conc. stream flow rate 185 ml/min. Two separate passes were made.

Pass	Volts	Ma. Start	Ma. End	ABS	COD	CL^-
Input sol.	--	--	-	9.0	95	298
1	30	300	200	9.0	86	276
2	30	300	200	8.5	91	248
% of Total Ref. Removed: (After 2 Passes)				5.5	4.2	16.7

One pass had very little effect and two passes, representing the use of two stacks in series, averaged only 8.8% removal of refractories, most of the renovation taking place in the Cl^-.

11) Renovation run, non-recirculated, voltage variation

In this three-pass run we used the same technique as in the preceding run. The same 18-liter volume of synthetic sewage was pumped through the stack three times, at the flow rates and voltages shown. In this run, we checked only for ABS reduction.

Pass	Flow, ml/min	Volts	ABS Input	ABS Output	Reduction	% Reduced
1	244	30	8.64	8.28	0.36	4.2
2	277	80	8.28	6.48	1.8	21.7
3	300	80	6.48	5.68	0.8	12.3

ABS reduction in passes 2 and 3 was encouraging and made apparent the improved renovation at the higher stack voltage. We decided to disassemble the stack at this point and examine the asbestos shields. They were found to be in excellent condition, although they appeared to have swollen to about twice their thickness when dry. The membranes themselves were also found to be in good condition.

The stack was reassembled without the asbestos shields in preparation for experiments in the sorption and desorption of ABS and COD from the unshielded membranes.

Unshielded Stack Runs

1) Continuing the work previously done with the unshielded stack, a series of single passes of synthetic sewage were made using 80V and an input flow rate of 600 ml/min; 10,000 mg/l NaCl solution was used as the concentrate stream, which was pumped at 175 ml/min. Analyses were made after each pass for ABS and at the beginning and end of the run for Cl^- and COD. The results of this multiple-pass run:

Pass No.	Ma, Start	Ma. End	ABS,mg/l	COD	Cl^-
0	-	-	8.6	125	256
1	330	420	8.1	-	-
2	460	460	7.6	-	-
3	440	440	7.2	-	-
4	440	420	5.1	-	-
5	390	380	3.9	-	-
6	380	330	3.0	-	-
7	320	220	2.3	-	-
8	290	250	1.6	-	-
9	220	220	1.3	-	-
10	210	210	0.9	46	28

These results are similar to those obtained previously and indicate that the membranes, in spite of the numerous sorbing cycles through which they had passed, were still in good sorbing condition.

2) The preceding run having deposited at least 0.4 meq of ABS in the stack membranes, we tried to regenerate the stack by the application of reverse current, hoping to get more of the ABS out of the membranes than we did in our previous attempt at reverse-current regeneration. The regenerative conditions used:

Conc. Sol: 2 liters, 10,000 mg/l NaCl
Volts: 80
Conc. Flow: 19 l/min
Dil. Sol: 2 liters, 1000 mg/l NaCl
Dil. Flow: 32 l/min.

The stack was subjected to 1-1/2 hours of reverse current. At the end of this time the concentration of ABS found in the dilute reservoir was only 3 mg/l; the conc. solution had fallen in concentration from 10,000 to 4,500 mg/l NaCl and the dilute solution had risen from 1000 mg/l to 14,250 mg/l NaCl. We could see here that there had been considerable salt transfer through the membranes but very little release of sorbed ABS.

The 2 liters of 3 mg/l ABS represent only 0.017 meq ABS. This 0.017 meq ABS is only 4.2% of the 0.4 meq ABS sorbed by the membranes during the preceding run. It is obvious that only a small percentage of the ABS sorbed can be removed by reverse current regeneration.

4.4 Discussion of Electrodialysis Test Results

The following appeared evident upon the conclusion of our experimental work with electrodialysis:

1. ABS is sorbed by an anion ion-exchange membrane under forward current and is not desorbed by reverse current.

2. ABS does not pass through a standard anion membrane under electrodialytic conditions.

3. ABS is not sorbed by a cation ion-exchange membrane under electrodialytic conditions.

4. ABS can be removed from an anion membrane upon which it has been sorbed by elution of the membrane with a 50/50 volume mixture of acetone and 1 N HCl[2].

5. The electrodeionizer stack is a modified form of electrodialysis stack capable of good renovation of ABS, COD and Cl^- from sewage.

6. The lab-scale electrodialysis stack is capable of reducing the refractory content of an effluent fed to it by approximately 5% in a single pass. It sorbs ABS irreversibly and therefore cannot be regenerated in the simplest possible way, by current reversal.

7. The employment of super-porous anion ion-exchange membranes, such as A-9 and A-11 discussed above, in electrodialysis does result in the transfer of small amounts of ABS through the membrane, but also results in excessive and unwanted water transfer.

It may be stated that the efficient use of electrodialysis as a method of sewage renovation depends upon facile transfer of relatively large organic ions through ion-exchange membranes, without accompanying excessive water transfer. We have not yet been able to accomplish this, and at present it appears that the use of conventional electrodialysis methods or equipment for the renovation of all classes of refractories from secondary sewage is impractical.

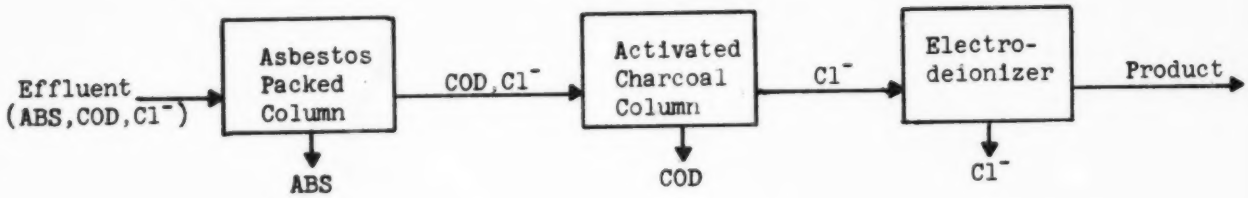
5.0 COMBINATIONS OF RENOVATION METHODS

5.1 Purpose

Electrodialysis is particularly adapted to the removal of dissolved salts from water or from sewage effluent. In the latter case, electrodialysis is more effective if ABS and COD are removed before the effluent enters the electrodialysis unit, thus preventing fouling of the ion-exchange membranes.

It was our purpose in this phase of the study to combine renovation methods in such a way that each of the three general classes of refractories, ABS, COD, and Cl^- would be removed by that renovation method best suited to its removal and that these methods would be employed in the most efficient order.

An example of this method is shown below:



Sorption of ABS by the cheap asbestos would relieve the load on the relatively expensive charcoal and the combined pretreatment by the two absorbents would allow the electrodialysis stage to operate against dissolved salts only.

5.2 Test Data

Three experimental runs were made with combinations of renovation methods:

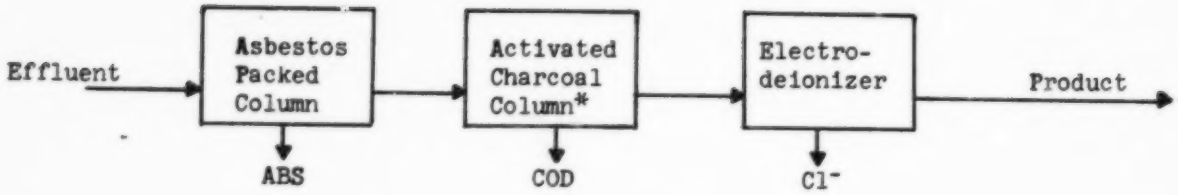
1) The first combination run was as described above:

	Leominster Input	After Asbestos	After Charcoal	After Cell	% Change Overall
COD, mg/l	45.0	23.5*	0	9.0	80
ABS, mg/l	4.2	0.6	0.7	0.7	83
Cl^-, mg/l	21.0	--	14.0	7.0	67

* We neglected to determine chloride ion content at this point, therefore the COD of 23.5 tested under "after asbestos" is actually uncorrected for Cl^-.

The asbestos did a good job of removing ABS from the effluent, as a bonus it removed some of the COD. The charcoal column did an excellent job of removing COD from the effluent. The electrodeionizer stack also did a good job, considering the low level of Cl^- fed to it.

2)



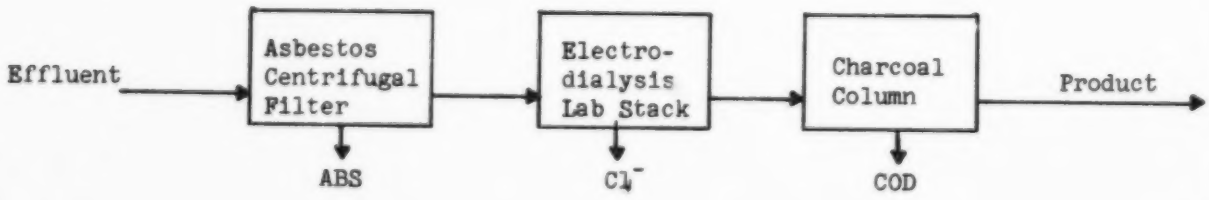
* Fisher activated cocoanut charcoal, 6-14 mesh, Cat. No. 5-685, $2.50/lb.
1-1/4 inch I.D. column, 12 inch bed depth, flow rate 250 ml/hr.

This experiment was the same as that described at 1) above except that the input was synthetic sewage rather than the settled but unfiltered Leominster effluent.

	Synthetic Sewage	After Asbestos	After Charcoal	After Cell	% Change Overall
COD, mg/l	117	82	0	7.0	94
ABS, mg/l	10	2	0.8	0.9	91
Cl^-, mg/l	213	167	64.0	1.4	99

The results of this test were excellent, the product water being nearly completely renovated. The slight increase in COD level after passage through the cell probably indicates pickup of organic matter from the beads or membranes.

3)



The asbestos centrifugal filter was prepared as described under Section 6 below.

	Leominster Effluent	After Asbestos	After Stack	After Charcoal	% Change Overall
COD, mg/l	41.0	17.7	9.8	0	100
ABS, mg/l	3.9	1.5	0.8	0.5	87
Cl^-, mg/l	25.0	38.0	1.8	3.6	86

The total throughput time on this experiment was only 1-1/4 hours as compared with 6-3/4 hours for runs Nos. 1 and 2. This is accounted for by the rapidity of the asbestos centrifuge as contrasted with the slow flow rate of the asbestos column. Renovation was again good.

5.3 Significance of Results

The results of the tests with combination of renovation methods are highly significant because the effectiveness of pitting individual renovation methods against individual refractory classes is so clearly demonstrated. It appears that the development of a single renovating device to handle all classes of refractories simultaneously will be much more difficult than the development of the several independent methods required.

6.0 MISCELLANEOUS

6.1 The Centrifugal Filter

The development of the centrifugal filter was prompted by a desire to speed up the flow of sewage effluent through asbestos packed columns. The centrifugal filter seemed like a good method of increasing filtration pressure without having to resort to pumps and pressure filters.

We used an International Equipment Company laboratory model chemical centrifuge with a five-inch diameter perforated bowl. The filter medium was prepared by pouring a water slurry of asbestos into the spinning centrifuge bowl. A flow rate of 2 liters per hour was easily attained with the centrifuge running at 3600 rpm as compared with a flow of only 30 ml/hr when a one-inch asbestos packed column was used.

First Trial

Both the Leominster Sewage effluent and our synthetic sewage 6568 were renovated by means of a single pass through the asbestos-lined centrifugal filter, prepared as above. The results of these two renovation runs are shown below:

Refractory Element	Leominster Effluent Input	Output	% Ren.	Synthetic Sewage 6568 Input	Output	% Ren.
ABS, mg/l	4.2	1.5	64	10	1.5	85
COD, mg/l	95	15.0	84	117	67.0	43
Cl^-, mg/l	23	27.0	0	213	178.0	16

A dark brown layer was deposited on the surface of the asbestos during the Leominster effluent run, indicating filtering of the turbidity found in that effluent. The much better COD reduction in the case of the Leominster effluent, as compared with the synthetic sewage, is probably due to the filtering off of turbidity.

The results of these two experiments were very encouraging. The asbestos centrifuge technique of sewage renovation could become very useful, particularly if some cheap, quick method of regenerating the asbestos could be found.

The ABS saturation point of an asbestos-lined centrifugal filter

Our primary purpose in the following experiment was to determine the total capacity or saturation point for ABS in the centrifugal asbestos filter. Our secondary purpose was to learn whether the filter could be regenerated after it had been saturated by ABS.

A fresh asbestos filter lining was prepared. We set up an 18-liter reservoir of 90 ppm ABS solution and its contents were pumped continuously through the asbestos filter at the rate of 2 l/hr. Periodic tests were made on the content of the reservoir to check its ABS concentration and thus determine when the saturation point was reached.

After 36 hours of continuous operation the filter became saturated with ABS. It had sorbed 495 mg of ABS, equivalent to 1.42 meq. The dry weight of the asbestos used to prepare the filter was 28.7 grams. This means that the asbestos has an ABS capacity of 0.0495 meq/dry gram. This is a low capacity when compared with the ABS capacity of an ion-exchange resin, which may run as high as 6 meq/dry gram.

The filter was regenerated by recirculating through it three separate 500-ml increments of 50/50 volume % acetone - 1 N HCl elutant solution. The results are as shown:

Increment No.	Mg/l ABS Pick-up	Circulating Time
1	380	1 hour
2	380	1/2 hour
3	188	1/2 hour

The recovery of ABS by elution was 1.36 meq, 95.7% of the 1.42 meq ABS calculated as input to the filter. At first the elutant solution would not circulate freely through the filter. Upon examining the surface of the asbestos, we found the filter surface to be coated with a slimey film. When this film was broken up, the circulation of elutant improved markedly and the regeneration proceeded normally.

It may be found, in further investigation, that most of the ABS sorption occurred in the inner surface of the asbestos filter lining and that the asbestos lying below the film formed on the surface may contain much unused ABS sorptive capacity. If this is the case, asbestos may possess a much higher ABS capacity than has been shown.

The Newspaper-lined Centrifugal Filter

We have been informed by the U.S.P.H.S. that filtration of ABS solutions through ordinary filter paper resulted in loss of ABS by sorption upon the paper. Leominster sewage effluent was filtered through a double Whatman No. 40 filter paper and then the filtered effluent was analyzed for COD and ABS content. The result:

Refractory	Before Filter	After Filter	% Change
COD, mg/l	45.0	77.0	71 (increase
ABS, mg/l	4.2	2.5	40

Filter paper is a good ABS sorber. COD rose because of cellulose pickup from the paper.

We went a little further along this line of investigation by preparing a column packed with water slurried newspaper. The slurry was prepared in a Waring Blender. The input to this newspaper column was 100 ml of a mixture containing 10 mg/l ABS and 400 mg/l NaCl. The analysis:

Refractory	Before Column	After Column	% Change
COD, mg/l	Negl.	164.0	increased
ABS, mg/l	10	1.6	84
Cl^-, mg/l	240	31.0	87

Newspaper has demonstrated good ABS and Cl^- renovating properties here.

A centrifugal filter was prepared using water slurried newspaper, using the same technique as in the case of the asbestos lined centrifugal filter. A 500-ml increment of synthetic sewage 6568 was passed through the filter at 2 liters/hr three times. The results of analysis of filtrate after the first and third passes are shown:

Refractory	Input	After 1 Pass	After 3 Passes
COD, mg/l	117	146	140
ABS, mg/l	10	5.0	5.0
Cl^-, mg/l	212	176	202

COD rose as expected, probably due to cellulose and ink pickup. ABS was reduced by 50% in the first pass but did not decline further with two more passes. The assumption from these results is that the ABS sorption capacity of newspaper is quite limited.

The Centrifugal Filter with Combined Asbestos-Charcoal Lining

A centrifugal filter was prepared in the usual manner by pouring into the spinning centrifuge a slurry consisting of equal volumes of asbestos and powdered activated charcoal*. 500 ml of synthetic sewage 6568 were put through the filter at the rate of 2 liters/hr. The filter output was analyzed. These analytical results are shown below, along with previously obtained results using asbestos alone as a filter medium.

Refractory	Input	Output with Combination	% Ren.	Output with Asbestos	% Ren.
COD, mg/l	117	50.3	57	67	43
ABS, mg/l	10	1.5	85	1.5	85
Cl^-, mg/l	212	174.0	18	178	16

It is apparent that the combination of charcoal and asbestos does not show any marked superiority to the asbestos alone.

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* Fisher 5-685, as previously used.

6.2 Column Tests

A few exchange column tests were made for various purposes during the course of our study.

Ion Exchange Column vs. Leominster Effluent

The ion-exchange beads used in this test were Dowex-21K (16-20 mesh), a quaternary ammonium strong base type, in chloride form. Dow classifies 21K as a high porosity type resin. The packed column was well rinsed with demineralized water before use. 250 ml of Leominster effluent was allowed to flow through the column. Flow time was 14 minutes. The results of our analysis:

Refractory	Before Column	After Column	% Change
COD, mg/l	45.0	15.0	67
ABS, mg/l	4.2	0.8	81
Cl^-, mg/l	21.0	103.0	390 (increase)

The renovation here was good, except for the Cl^-. The rise in Cl^- level can be attributed to displacement of Cl^- from the resin by an anion in the effluent having greater affinity for the resin than Cl^- (NO_3^-, HSO_4^-, HSO_3^-, HCO_3^-), or by displacement of the Cl^- from the resin by an organic ion.

Asbestos Columns

1) The column used in this test was prepared by pouring into it a water slurry of Carey I-30 asbestos made in the Waring Blender. The water was allowed to drain from the slurry before the column was used. Before use, the column was rinsed twice with demineralized water.

250 ml of Leominster effluent was poured through this column, the time for complete throughput totalling 9-1/2 hours. The analytical results:

Refractory	Input	Output	% Change
COD, mg/l	45.0	45.0	--
ABS, mg/l	4.2	0.7	83
Cl^-, mg/l	21.0	*	--

* Unintentionally failed to analyzed for chloride here, therefore the COD value of 45 mg/l given under "output" is actually uncorrected for chloride and is actually lower than shown. The ABS renovation was excellent.

2) A column was prepared as in (1) above and 100 ml. increments of 100 mg/l ABS - 400 mg/l NaCl were passed through it successfully until 118 increments had passed through. At this point, the output contained 6.7 mg/l ABS, demonstrating that the column still retained considerable sorption power for ABS. It was noted that the pass-through time of the final increment was more than seven hours, compared with a pass-through time for the first increment of less than two hours. The explanation of this may be that the asbestos, with its complex molecular structure, traps ABS in much the same way that an anion membrane does, by the formation of ABS micelles within the fibrous structure of the asbestos. The fibrous structure swells, as did the membrane under similar conditions, when the ABS level rises. As a result of this swelling, liquids move through the asbestos mass with greater difficulty, resulting in longer pass through times.

6.3 Preparation of Pure ABS

The ABS used in this study came in the form of various samples:

1) Standard Alkylbenzene Sulfonate - Lot #3 - June 1961

ABS:	54.8%	Association of American Soap and Glycerine Products, Inc. 295 Madison Avenue New York 17, New York
Na_2SO_4:	40.3%	
Free Oil:	0.5%	
NaOH:	1.3%	
Na_2CO_3:	0.7%	
H_2O:	2.6%	
pH	11.0	

2) Santomerse 85, Surface Active Agent, Anionic Surfactant, 10 mesh; Monsanto Chemical Company, St. Louis, Missouri. 85% ABS, 14% inorganic salts (principally sodium sulfate) and 1% water.

3) Trepolate F-95 - 95% ABS, 5% salts and water.
Treplow Chemical Company, a subsidiary of the Richardson Company, 100 New Street, Paterson, New Jersey.

Instructions were received in a private communication from W.B. Bennet of Monsanto for preparation of pure ABS from Santomerse 85.

Dissolve Santomerse 85 in ten times its weight of 80% (by volume) isopropyl alcohol and filter off the inorganic portion. The inorganic portion should be further extracted with a fresh portion of the alcohol to recover the less soluble isomers of ABS. The combined alcohol solutions may be dried on a steam plate to give a plastic solid which on cooling becomes brittle and very hygroscopic.

Using the above procedure, ABS was prepared which assayed (by the methylene blue complex method of analysis) at better than 98% purity.

Whenever ABS solutions were prepared, the ABS content of the product used to prepare the solution was taken into account. When solutions of high concentration, such as 800 mg/l - 2000 mg/l ABS, were prepared, these solutions were often cloudy in appearance. This may be attributed to the salting out effect of the salts contained in solution as a consequence of using ABS products which contain salts to prepare the solutions. Much less cloudiness was noted when the Trepolate F-95 was used to make up ABS solutions than when the other two products were used, in fact, a clear 10,000 mg/l ABS stock solution could be prepared with Trepolate F-95.

6.4 Conductivity of ABS in Aqueous Solution

To determine what contribution ABS makes to the conductivity of solutions of which it is a part, the conductivity of a 9 mg/l solution in demineralized water of the pure ABS was prepared. Using an Industrial Instruments Model RC-1B conductivity bridge, the conductivity of the solution was found to be negligible.

The conductivities of a 400 mg/l NaCl solution and a 400 mg/l NaCl solution containing 10 mg/l ABS were compared with the conductivity bridge. Both read 490 mho/cm, indicating that the contribution to the conductivity of the solution of the ABS was too small to measure.

6.5 The Effect of ABS Sorption upon Membrane Resistivity

A section of Ionics' standard anion membrane was tested for resistivity and found to read 135.5 ohms (16.7 ohm-cm^2). After an overnight immersion in a 2000 mg/l ABS solution, its resistivity rose to 42,000 ohms (5200 ohm-cm^2).

Observations taken during this study indicate that the membrane section was probably not saturated with ABS after its immersion overnight in the ABS solution. Therefore, its resistivity would be even higher, probably much higher, at the ABS saturation point.

7.0 CONCLUSIONS AS TO THE TECHNICAL AND ECONOMIC FEASIBILITY OF RENOVATION METHODS

7.1 Ion Exchange Column Method

This process shows promise for the removal of ABS and COD from secondary sewage effluent. It has not been shown that dissolved salts can be simultaneously removed from the effluent.but they do not affect the ABS capacity of the resin.

The efficiency of the ion exchange column renovation process depends upon several factors, none of which has been sufficiently investigated here to warrant firm conclusions as yet. These factors are:

1. Sorption rate of the resin used.
2. Sorption capacity of the resin used.
3. Resistance of resin to chemical and mechanical attrition.
4. Ease of regeneration of the resin.
5. Degree of resin regeneration possible.

Abrams and Lewon[2] have discussed the cost of removing ABS from sewage effluent by passage through ion exchange beds. They employed A-102D resin, a product of the Chemical Process Co., Redwood City, California (now Western Division of Diamond Alkali Co.). This resin has an ABS sorptive capacity of 350 grams of ABS per liter of resin. Based upon an influent 2 mg/l ABS, they calculated that resin replacement cost would be about 5.4 cents per thousand gallons of sewage treated. Regeneration costs would be approximately 0.5 cents/kgal., if this procedure could be used.

We have made a similar calculation, employing the following assumptions:

1. The ABS sorptive capacity of the ion exchange resin used (A18) is 2000 gms of ABS per liter of resin or 56,000 gms/cu.ft.
2. The ABS content of the input sewage effluent is 5 mg/l.
3. The regeneration step restores the resin to 90% of its original capacity.
4. The cost of A18 resin is $100 per cubic foot.
5. The cost of regenerant solution is $0.50 per gallon.
6. The ratio of regenerant solution to sewage treated is 1:100,000.
7. The number of passes possible is 10.
8. Reduction of ABS content of the input sewage effluent will be 95%.

Consider an ion exchange bed containing 1 cubic foot of A18 resin. This amount of resin would be capable of renovating 2,940,000 gallons of sewage effluent containing 5 mg/l ABS, before exhaustion in the first pass and could then be regenerated to 90% of its original ABS capacity. Taking the ABS capacity of the resin after 4 regenerations as the average, we take 65% of original capacity as our working capacity.

56,000 gms/cu.ft. × 0.65 = 36,400 gms/cu.ft. average ABS capacity.

Gallons renovated per pass at this capacity = 1,910,000.

Cost of resin replacement per 1000 gal. = 5.2 cents.

1,910,000 gallons × 10 = 19,100,000 gallons processed in ten passes.

Regenerant consumed in 9 regenerations = 19.1 × 9 = 172 gallons.

Total cost of resin	= $ 100
Total cost of regenerant, 172 gallons @ $.50	= $ 86
Total Cost ($86 + $100)	= $ 186
Cost regeneration per thousand gallons ($86/19,100)	= .45 cents
Total cost regeneration per thousand gallons ($186/19,100)	= .98 cents

This estimate is based upon laboratory data only. It should be confirmed by large scale tests.

7.2 Electrodialysis

An estimate of the cost of removing ABS from sewage effluent by means of electrodialysis has been made, using as a cost reference "Some Practical 1959 Advances in Electric Membrane Demineralization"[4] by W.E. Katz of Ionics, Inc.

Our best data, using the laboratory scale electrodialysis stack, shows an ABS reduction of 20% per pass. Three passes would be required to attain a 50% reduction in ABS concentration.

It is estimated[5] that a plant to treat 10×10^6 gallons/day of 4000 mg/l brackish water to produce 500 mg/l product water would cost 2/3 of the cost of a 2×10^6 gallons/day plant, on a per 1000 gallon basis. Further reductions in cost by a factor of from 2 to 4 are envisioned in the next five years for plants in the 10×10^6 to 100×10^6 gallons/day range.

The capital cost of a 2×10^6 gallons/day plant at present is about $\$1.3 \times 10^6$. If, by taking 2/3 of the increase in electrodialysis stack costs, we assume a multiplying factor of 3 in going from a 2×10^6 gallons/day plant to a 10×10^6 gallons/day plant, the capital cost of the latter would be about $\$4.0 \times 10^6$. Total water costs for the 2×10^6 gallons/day plant include 25 year amortization; 0.2/year membrane replacement, 1 cent/KWH power cost, labor, overhead, filtration, chemical and maintenance costs. This amounts to 57.5 cents per 1000 gallons treated. Electrical energy varies from 4.9 cents/1000 gal. for a 1000 mg/l plant* to 26 cent/1000 gal. for a 4000 mg/l plant*. Present laboratory data indicate that electrical energy consumption for ABS removal will be approximately 4 to 5 times that of the 1000 mg/l figure at best, or close to that for the 4000 mg/l plant.

A larger plant would reduce maintenance and amortization costs per gallon, (except for membranes) which represent 30.4 cents/1000 gallons or 53% of the total cost. While it is doubtful that maintenance and amortization costs could be reduced by 60% of their present levels on a 1000 gallon basis, a 40% reduction might be achieved, i.e., $30.4 \times 0.4 = 12.2$ cents/1000 gallons reduction.

An ABS system would have additional chemical and maintenance costs, e.g., membrane regeneration, which might add an additional 5 cents/1000 gallons cost.

Thus, a larger plant might reduce the overall treatment cost by 7.2 cents/1000 gallons, when compared to a 4000 mg/l brackish water plant. Summarizing, approximate costs would be:

Capital cost:	\$ 4,000,000
Cost/1000 gal:	\$ 0.50

Any reduction in power cost toward the 1000 mg/l plant would, of course, lower the cents/1000 gallon cost.

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* a "1000 mg/l plant" is one which is designed to treat a brackish water containing an average TDS of 1000 mg/l.

It must be kept in mind that the above estimate is for an electrodialysis plant designed specifically for the reduction of ABS concentration. Such ABS removal by electrodialysis would, of course, simultaneously demineralize the feed, but to an unnecessarily low salt content and at a cost which would not reflect the current economics for simple demineralization by electrodialysis. Estimated costs for the production of 2×10^6 GPD fresh water are shown in Table III, which is taken from Katz' paper. They are less than 20 cents/Kgal. for water with a salinity of typical sewage effluent.

TABLE III

ESTIMATED COSTS FOR PRODUCTION OF 2,000,000 GPD FRESH WATER (500 ppm as NaCl) FROM THREE DIFFERENT BRACKISH WATERS BY IONICS' MARK III EQUIPMENT (cents/1000 gallons)

Basis

Feed water temperature - 85°F
Anions predominantly chloride
Electrical energy cost - 1.0 cent/kwhr
Membrane replacement rate - average 1/5 per year
Amortization basis - 25 year, 5% (7.1% per year)
Maintenance costs other than membranes - 1.5% per year of capital
Labor allowance - 2 hrs. per day plus 100 man hours per stack year @ $4/hr., including overhead

		Case 1		Case 2		Case 3
Feed water total dissolved solids		1000 ppm		2000 ppm		4000 ppm
Number of stacks		8		16		24
Total capital costs		$450,000		$850,000		$1,300,000
A. Operating Costs						
(1) Electrical energy	4.9¢		13.4¢		26.0¢	
(2) Chemicals	2.5		2.5		2.5	
(3) Pre-filtration	3.0		3.0		3.0	
Total operating costs		10.4¢		18.9¢		31.5¢
B. Maintenance Costs						
(1) Membranes	3.0¢		6.0¢		9.0¢	
(2) Other maintenance	0.9		1.8		2.7	
(3) Labor	0.8		1.3		1.7	
Total maintenance costs		4.7¢		9.1¢		13.4¢
C. Amortization		4.4¢		8.3¢		12.6¢
Total Water Costs (cents/1000 gallons)		19.5¢		36.3¢		57.5¢

8.0 REFERENCES

(1) Columnar Ion Exchange - see Dowex: Ion Exchange, the Dow Chemical Company, Midland, Michigan (1958).

(2) The Removal of Alkylbenzene Sulfonate from Water by Chloride Cycle Ion Exchange - Irving M. Abrams and Sidney M. Lewon, Journal of the American Water Works Association, 54, No.5., 537 (1962)

(3) City of Leominster, Massachusetts sewage treatment plant. This secondary sewage treatment plant treats the sewage from a city of 25,000 people, handling about 4×10^6 gpd at present. The raw sewage is first settled, then aerated and treated with activated sludge. Samples of the effluent from this plant were taken at the point of discharge into the Nashua River. Analysis of the settled effluent showed

COD:	42 mg/l
ABS:	4.2 mg/l
Cl^-:	21 mg/l

(4) Some Practical 1959 Advances in Electric Membrane Demineralization, W.E. Katz, Ionics, Inc., ACS Advances in Chemistry Series, Vol 27.

(5) Synthetic Sewage 6568

Prepared as follows:

18 ml 10,000 mg/l ABS (95% active) solution
600 ml 1 g/l benzoic acid in water solution
600 ml 1 g/l Isopropanol in water solution
150 ml 40,000 mg/l NaCl in water solution
Water to make 18 liters

The above formulation gives a typical analysis as shown:

COD, mg/l	117
ABS, mg/l	10
Cl^-, mg/l	213

While benzoic acid and isopropanol are not refractories in the sense that they will resist a secondary sewage treatment such as activated sludge, they do represent two of the most important organic refractories, acids and alcohols. They were selected also because they are water soluble and capable of being completely oxidized by the COD method used.

(6) Analytical Methods Used.

See Standard Methods for the Examination of Water and Waste Water, 11th Edition, 1960.

a) methylene blue complex method for ABS, p.246
b) Mohr method for chloride, p.78
c) acid-chromate method for COD, p.399

All COD values given in this report have been corrected for ABS and Cl^- by means of the following correction factors:

COD, corrected value = original value -(mg/l Cl^- × .23)
COD, corrected value = original value -(mg/ABS × 1.8)